BIS(DIPHENYLPHOSPHINOETHYL)SULPHIDE AS A CHELATING LIGAND

A structural study of some transition metal complexes

LARS FÄLTH

Lund 1976

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Avhandlingen kommer att försvaras vid offentlig disputation å Kemicentrum, hörsal D, lördagen den 8 maj 1976 kl. 10.15.

av

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LUND 1976

UNIV.
LEIDEN
BIBL.

Fälth, L. (1976)

Thesis. Inorganic Chemistry.

University of Lund, Lund, Sweden.

ISBN 91-7222-156-9

ABSTRACT

Three metal complexes of the potentially tridentate ligand bis(diphenylphosphinoethyl)sulphide, $(C_6H_5)_2P(CH_2)_2S(CH_2)_2P(C_6H_5)_2$, have been investigated by X-ray diffraction methods, viz. the compounds HgI_2PSP, $(AgClPSP)_2$ and NiI_2PSP (the formula of the ligand is abbreviated to PSP).

In the structures of the mercury and silver complexes there are large rings; eight-membered in the case of mercury and, in the case of silver, two linked ten-membered rings. The formation of such rings is quite uncommon and was therefore not foreseen. Five-membered rings are common. Two of these, fused together, form part of the structure of the nickel complex. In the mercury and silver salts the ligand molecules are bonded to the metal atoms via the two phosphorus atoms, in the nickel compound via both the phosphorus atoms and the sulphur atom.

The eight- and ten-membered rings may be explained from the kinetics of their formation.[31] Interatomic distances and angles in these structures are compared with those in the complex diiodo[bis(triphenylphosphine)]mercury(II) which was also investigated.

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1. INTRODUCTION

The purpose of the present article is to summarize some results forming part of the project Structures of Complexes between Metal Halides and Phosphinothioethers or Related Ligands, the structural works being reported in the following papers:

I. Aurivillius, K. and Fälth, L. The crystal and molecular structure of diiodo[bis(diphenylphosphinoethyl)sulphide] mercury(II), $HgI_2P_2SC_{28}H_{28}$, Chem. Scr. 4 (1973) 215.[1]

II. Aurivillius, K., Cassel, A. and Fälth, L. The crystal and molecular structure of dimeric chloro[bis(diphenylphosphinoethyl)sulphide]silver, $(AgClP_2SC_{28}H_{28})_2$, Chem. Scr. 5 (1974) 9.[2]

III. Fälth, L. The crystal and molecular structure of diiodo-[bis(diphenylphosphinoethyl)sulphide]nickel(II), $NiI_2P_2SC_{28}H_{28}$, Chem. Scr. (1976), in press.[3]

IV. Fälth, L. The crystal and molecular structure of diiodo-[bis(triphenylphosphine)]mercury(II), $HgI_2[P(C_6H_5)_3]_2$, Chem. Scr. 9 (1976) 71.[4]

Substituted phosphines joined by aliphatic chains of different lengths, with a methylene group of the chain sometimes replaced by e.g. S, $P(C_6H_5)$, have been synthesized and characterized at ETH, Zürich, Switzerland, by several authors.[6,7,8] Complexes between these ligands and salts of transition metals including mercury have been prepared in order to study the "hard" and "soft" characters of the metal ions.[6]

In some cases the coordination of the ligands around the central metal atom could be determined by solution chemistry and IR spectra;[6]

in other cases more than one possibility remained. To elucidate the geometries of some phases of this type in the solid state G. Schwarzenbach, at the end of the sixties, asked K. Aurivillius to study, by diffraction methods, the crystal structures of some compounds of the ligand bis(diphenylphosphinoethyl)sulphide, $[(C_6H_5)_2P(CH_2)_2]_2S$, with halides of mercury(II) and silver, respectively.

As these first structural works gave interesting results an increased collaboration followed: and, as a consequence of these results compounds of appropriate metal complexes with other ligands, related to bis(diphenylphosphinoethyl)sulphide, have been synthesized in our laboratory at the Chemical Center. The single crystals used for the data collections of the compounds whose structures are reported in the papers I-IV were kindly supplied by G. Schwarzenbach.

1.1 Abbreviations

In the text the following abbreviations are used:

$(C_6H_5)_2P(CH_2)_5P(C_6H_5)_2$ ..... PCP

$(C_6H_5)_2P(CH_2)_2S(CH_2)_2P(C_6H_5)_2$ ..... PSP

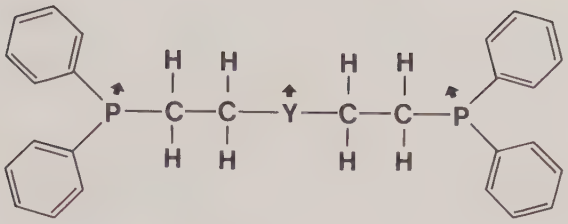
$(C_6H_5)_2P(CH_2)_2O(CH_2)_2P(C_6H_5)_2$ ..... POP

$(C_6H_5)_2P(CH_2)_2NH(CH_2)_2P(C_6H_5)_2$ ..... PNP

$P(C_6H_5)_3$ ..... PPh_3

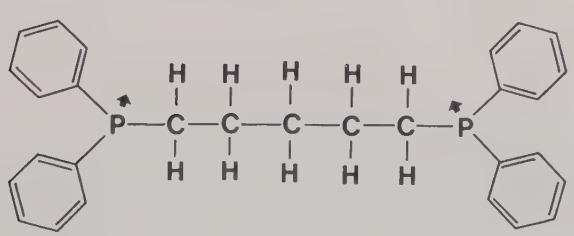
2. LIGANDS

PYP, Y=O,S,NH



The PYP ligands with Y=O,S,NH are potentially tridentate with two phosphorus and oxygen, sulphur or nitrogen as chelating atoms. These atoms, having lone pairs of electrons, can form π-bonds with metal acceptor orbitals.

PYP, Y=CH_2

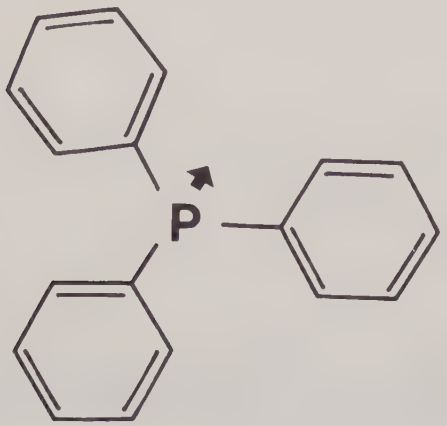


This ligand is bidentate with the two phosphorus atoms as chelating atoms.

The crystal structures of the PYP ligands themselves have not yet been determined.

PPh_3

Triphenylphosphine is commercially available. Its structure has been determined by Daly.[9] The coordination of the phosphorus atom can be described as a tetrahedron with the lone pair of electrons at one vertex.



3. PREPARATIVE WORK

In connection with the syntheses of related ligand molecules, the ligand molecule bis(diphenylphosphinoethyl)sulphide, (PSP), has been prepared, following the method given by Degischer:[6] Tertiary phosphines can be prepared by reaction between an alkalialkylphosphine and an alkylhalide dissolved in e.g. ether or toluene:

$$R_2PMe + RX \xrightarrow[-MeX]{} R_3P$$

Bis(diphenylphosphinoethyl)sulphide is prepared in an analogous way:

$$2Ph_2PNa + Cl(CH_2)_2S(CH_2)_2Cl \xrightarrow[-2NaCl]{} Ph_2P(CH_2)_2S(CH_2)_2PPh_2$$

For accurate X-ray work, single crystals of suitable size must be prepared and, for these sparingly soluble metal complexes, this has been the main difficulty. Our preparations, following the descriptions given by Degischer, in most cases resulted in microcrystalline products.
A short account of the methods given by Degischer is presented below.

3.1 Synthesis of $(AgXPSP)_2$

Equal amounts of silver nitrate and PSP are dissolved in acetonitrile and an equivalent amount of tetraethylammonium-chloride is dissolved in a second portion of the same solvent.

The two solutions are mixed gently heated:

$$2AgNO_3 + 2PSP + 2Et_4NCl \rightarrow$$
$$\rightarrow (AgClPSP)_2 + 2Et_4NNO_3$$

3.2 Synteses of HgI_2PSP and $HgI_2(PPh_3)_2$

Because HgI_2 is very sparingly soluble in acetonitrile, HgI_2PSP and $HgI_2(PPh_3)_2$ can not be made in the same way as $(AgClPSP)_2$. However, due to complex formation, HgI_2 is soluble in an acetonitrile solution of tetraethylammoniumiodide. HgI_2PSP is formed by adding PSP dissolved in acetonitrile:

$$HgI_2 + Et_4NI \rightarrow (Et_4N)_2HgI_4$$
$$(Et_4N)_2HgI_4 + PSP \rightarrow HgI_2PSP + 2Et_4NI$$

$HgI_2(PPh_3)_2$ is prepared in a similar way:

$$(Et_4N)HgI_4 + 2PPh_3 \rightarrow HgI_2(PPh_3)_2 + 2Et_4NI$$

3.3 Synthesis of NiI_2PSP

When a solution of NiI_2 in butanol is added to an equal amount of PSP dissolved in a mixture of benzene and butanol, NiI_2PSP is precipitated as dark green crystals:

$$NiI_2 + PSP \longrightarrow NiI_2PSP$$

4. DETERMINATION OF THE STRUCTURES

The structure determinations are based on three-dimensional intensity data. The intensity measurements were made either with the multiple film technique using an integrating Weissenberg camera or with a single crystal diffractometer (Enraf-Nonius Cad 4). For details, see Table 1.

Table 1. Intensity data collections

Complex	Method	Radiation	No. of recorded reflexions	No. of reflexions used in the final calculations
HgI_2PSP	film	CuK (Ni-filter)	1337	1337
$(AgClPSP)_2$	film	CuK (Ni-filter)	2038	2021
NiI_2PSP	diffr.	$CuK\alpha_1$	6306	3201
$HgI_2(PPh_3)_2$	diffr.	$CuK\alpha_1$	6597	4210

Space groups and preliminary cell dimensions were in all cases determined from rotation and Weissenberg photographs. More accurate cell parameters were obtained from least-squares refinements of $\sin^2\theta$-values taken from Guinier powder diffractograms or from the accurate settings of some reflexions measured on the single crystal diffractometer. The densities were measured by flotation. Some crystal data are presented in Tables 2 a-d. For HgI_2PSP the intensities of the observed reflexions were estimated visually, by comparison with a calibrated scale, while for $(AgClPSP)_2$ they were measured optically with a micro densitometer (Nonius).

Table 2a

HgI_2PSP Space group no. 2 $P\bar{1}$

F.W.= 913.0	α = 91.23(5)°	D_{obs} = 2.02 g cm^{-3}
a = 9.421(5) Å	β = 92.27(7)°	z = 2
b = 10.237(5) Å	γ = 115.08(2)°	D_{calc}= 2.03 g cm^{-3}
c = 17.097(12) Å	V = 1491 $Å^3$	μ = 281 cm^{-1}

Table 2b

$(AgClPSP)_2$ Space group no. 2 $P\bar{1}$

F.W.= 1202.0	α = 95.61(3)°	D_{obs} = 1.42 g cm^{-3}
a = 11.560(4) Å	β = 101.98(4)°	z = 1
b = 10.063(2) Å	γ = 93.24(3)°	D_{calc}= 1.43 g cm^{-3}
c = 12.045(6) Å	V = 1360 $Å^3$	μ = 86 cm^{-1}

Table 2c

NiI_2PSP Space group no. 14 $P2_1/c$

F.W.= 771.1		D_{obs} = 1.80 g cm^{-3}
a = 12.781(1) Å	β = 106.04(1)°	z = 4
b = 31.194(8) Å		D_{calc}= 1.78 g cm^{-3}
c = 7.4935(7) Å	V = 2781 $Å^3$	μ = 201 cm^{-1}

Table 2d

$HgI_2(PPh_3)_2$ Space group no. 14 $P2_1/c$

F.W.= 979.0		D_{obs} = 1.91 g cm^{-3}
a = 19.2898(8) Å	β = 111.800(5) °	z = 4
b = 10.2797(5) Å		D_{calc}= 1.93 g cm^{-3}
c = 18.2766(8) Å	V = 3365 $Å^3$	μ = 270 cm^{-1}

The intensity data were all corrected for Lorentz, polarisation and absorption effects. For $HgI_2(PPh_3)_2$ a correction for secondary extinction was applied but it did not improve the result.

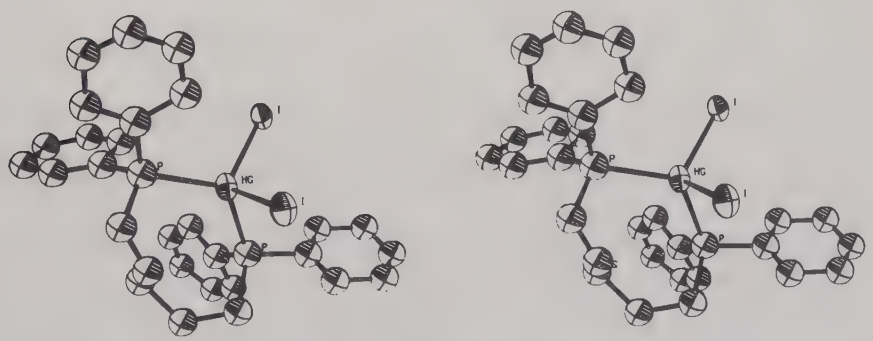
The heavy atom positions in the structures of HgI_2PSP, $(AgClPSP)_2$ and $HgI_2(PPh_3)_2$ were all determined from the three-dimensional Patterson function. The positions of the nickel and the iodine atoms in the structure of NiI_2PSP were determined by means of symbolic addition methods, using the computer program GAASA.[10] The positions of the non-heavy atoms, except the hydrogen were obtained from successive difference Fourier syntheses. Scattering factors, for the neutral atoms were used in the calculations. They were taken from Cohen,[11] Cromer and Waber[12] and Hanson, Herman, Lea and Skillman.[13]

5. BRIEF DESCRIPTIONS OF THE DETERMINED STRUCTURES

In this chapter only short accounts of the structures of the compounds listed in Table 1 will be made. More detailed descriptions have been made in references 1-4.

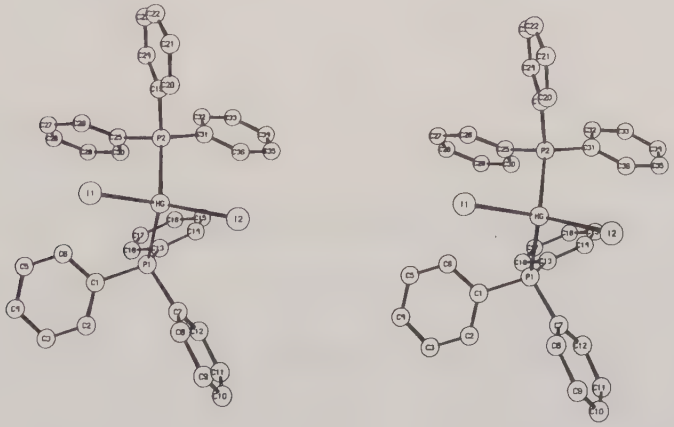
5.1 HgI_2PSP

The structure of HgI_2PSP consists of discrete monomeric molecules HgI_2PSP. The mercury atom is four-coordinated: bonded to two iodine and to the two phosphorus atoms of the PSP ligand. PSP thus functions as a bidentate ligand, the sulphur atom being uncoordinated. This causes the formation of an eight-membered ring $Hg(PC_2)_2S$. The coordination polyhedron is a distorted tetrahedron, with bond angles between 97° and 123°. There is a small difference, 0.10 Å, between the two mercury-iodine distances, which are 2.858(4) and 2.759(4) Å. The distance Hg-S=3.71(1) Å is a non-bonded distance, which will be discussed below (p. 22).



5.2 $HgI_2(PPh_3)_2$

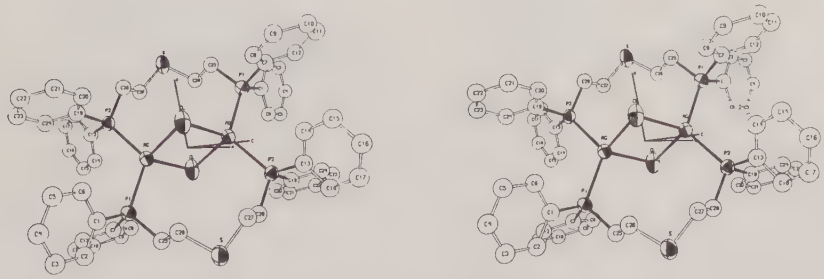
The structure of $HgI_2(PPh_3)_2$ consists of monomeric molecules. The mercury atom is tetrahedrally coordinated by two iodine and two phosphorus atoms. The distortion of the tetrahedron is not as large as in the structure of HgI_2PSP, the bond angles varying between 105° and 113°. There is only a small difference, about 0.03 Å, in the Hg-I distances, 2.733(1) and 2.763(1) Å.



5.3 $(AgClPSP)_2$

The structure of $(AgClPSP)_2$ consists of dimeric molecules. The ligand acts as a bidentate, bridging ligand with the two phosphorus atoms coordinating different silver atoms. The two ligands are linked via two Ag bridges. As in the structure of HgI_2PSP the sulphur atoms is uncoordinated. The silver atoms are also joined by a double chlorine bridge, the silver and chlorine atoms forming an almost perfect square. Two ten-membered rings $Cl(AgPC_2)_2S$ occur in the structure.

The coordination around silver is tetrahedral, with the polyhedron a little less distorted than in the structure of HgI_2PSP. The bond angles vary between 104° and 118°.



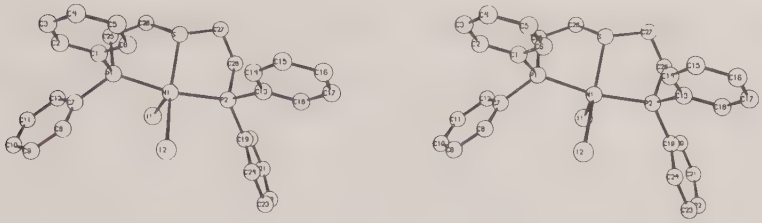
5.4 NiI_2PSP

The structure of NiI_2PSP is also composed of separate molecules which in this case are monomeric. The ligand PSP is tridentate, with the sulphur also coordinated to the metal atom. The nickel atom is thus five-coordinated: by two iodine atoms, two phosphorus atoms and one sulphur atom. The coordination polyhedron is intermediate between a square pyramid and a trigonal bipyramid. The Ni-I distances are significantly different, 2.794(2) and 2.542(2) Å, which is probably a result of the sulphur coordination.

When the coordination polyhedron is described as a square pyramid one iodine, one sulphur and two phosphorus atoms form the base and the second iodine the apex of the pyramid.

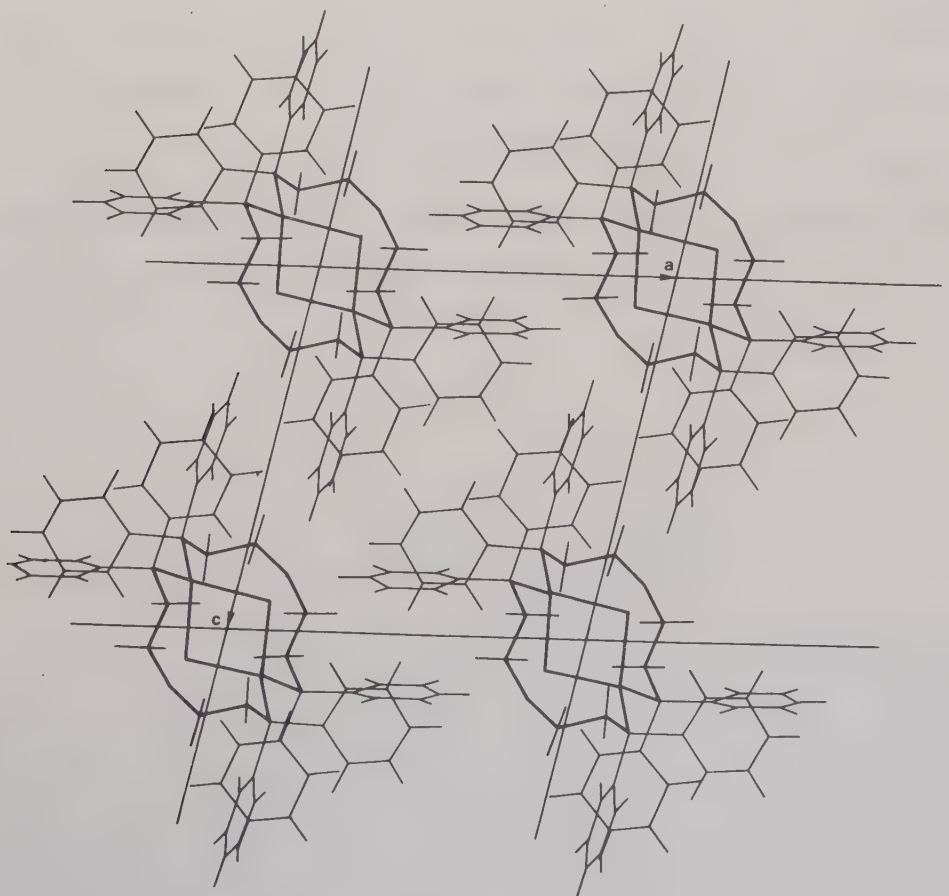
In the trigonal bipyramid description the sulphur and the two iodine atoms form the equatorial plane, and the two phosphorus atoms are in the axial positions. One of the equatorial angles

(< S-Ni-I) is much larger than the other two. This is common in 3d metal complexes with chelating ligands.[26,27,28]



As no short intermolecular distances less than the sums of the appropriate van der Waal's radii occur, the discussed structures consist of the packings of discrete molecules, monomeric or dimeric.

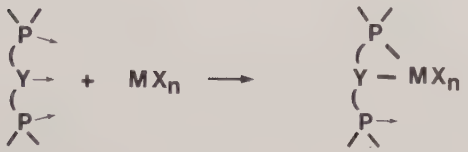
The positions of the hydrogen atoms in the structures are not investigated, but as an example of the packings the $(AgClPSP)_2$ structure has been chosen:



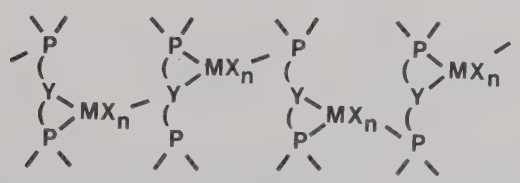
6. FORMATION OF RING SYSTEMS WITH THE TRIDENTATE PHOSPHINE LIGANDS PSP, POP AND PNP

6.1 Single five-membered ring

A single five-membered ring is formed if the metal atom is coordinated by two adjacent chelating atoms in the ligand.

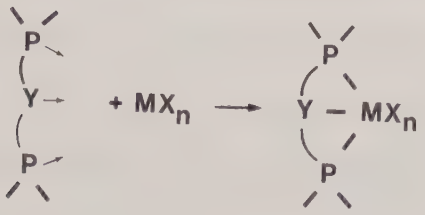


This type of ring formation was proposed by Degischer[6] as one alternative for the coordination of mercury in HgI_2PSP. However, it is not observed with PSP, POP or PNP ligands. The long tail, C-C-P-Ph_2, which would result in this case will reduce the stability of the complex. If this type of ring is formed, it will certainly occur in connection with some kind of polymerization of the complexes, e.g.:



6.2 Double five-membered ring

A double five-membered ring will occur when all the chelating atoms in the ligand molecule coordinate the same metal atom:



This type of ring formation is found in NiI_2PSP [3] and $NiBr_2PNP$ [14] but not in $NiCl_2POP$.[15]

According to Schwarzenbach, Leden, Ahrland, Chatt and Davies,[16,29,30] the metals can be divided in two groups, hard metals (a) and soft metals (b). The a-metals are those which form the most stable complexes with the first member in a group of the periodic table. The b-metals form the weakest complexes with the first member of the group:

$$F < Cl < Br \ll I$$

$$O \ll S \approx Se \approx Te$$

$$N \ll P > As > Sb > Bi$$

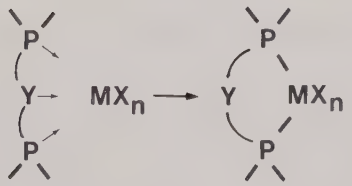
The a-metals are weakly polarizable (hard) and take part in complexes with predominantly electrostatic bonds. The b-metals are more polarizable and are to be found in complexes with more covalent bonds.

According to the above-mentioned authors, nickel(II) has a typical b-nature.

The boundary in the periodic table for the central chelating atom to coordinate nickel seems to be between oxygen and sulphur. When the central chelating atom does coordinate the metal atom one of the nickel-halide distances is increased. It seems that sulphur and nitrogen but not oxygen can compete with the halide atoms at the π-accepting metal orbitals.

6.3 Eight-membered ring

An eight-membered ring will occur when the outer chelating atoms, but not the central one, coordinate the metal atom:



This type of ring is found in $NiCl_2POP$ [15] and in HgI_2PSP.[1] This ring in the structure of HgI_2PSP coincides with the second alternative proposed by Degischer.[6]

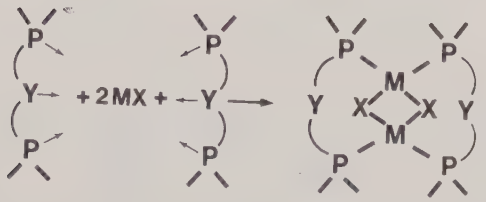
6.4 Fused ten-membered rings

Concerning the fused ten-membered rings in $(AgXPSP)_2$, see 7.1.

7. DIMERS AND POLYMERS

When the chelating atoms of the ligand coordinate different metal atoms dimers or polymers will occur.

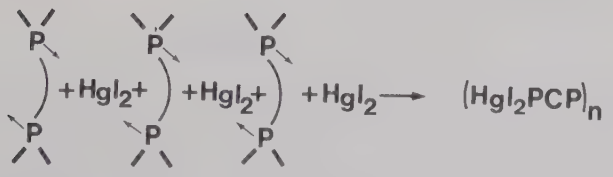
7.1 Dimerization



This type of dimerization is found in the silver complexes with PSP, viz. $(AgClPSP)_2$, $(AgBrPSP)_2$ and $(AgIPSP)_2$.[2,17] Besides the bridging by the PSP-ligand, halogen atom bridges are also formed.

7.2 Polymerization

To our knowledge no polymerization with PSP, POP or PNP ligands has been observed. However, the complex between HgI_2 and the bidentate ligand PCP is a polymer. The crystal structure of HgI_2PCP [5] contains endless chains of formula $(HgI_2PCP)_n$.



8. BOND DISTANCES

In this chapter distances between the metal atoms and their coordinated ligand atoms are discussed. These distances, obtained in the structures of the complexes (1-4), will be compared with corresponding values in related compounds.

8.1 Mercury to iodine distances

Complex	Hg-nI Distances (Å)	n	Difference Δ (Å)	Δ/σ(Δ)	Ref.
HgI_2PSP	2.858(4) 2.759(4)	1 1	0.099	18	1
$HgI_2(PPh_3)_2$	2.733(1) 2.763(1)	1 1	0.030	21	4
HgI_2PCP	2.771(1)	2			5
HgI_2	2.78	4			18

One of the distances, 2.858(4) Å is much longer than the others. This may be caused by a weak influence of the sulphur atom on mercury. The distance mercury to sulphur is 3.71(1) Å, found in the structure of $Hg(SCN)_2(PPh_3)_2$.[19] The influence of the sulphur atom of the ligand is more obvious in some five-coordinated Ni(II)-complexes, e.g. NiI_2PSP cf. p. 25.

In the complexes $HgI_2(PPh_3)_2$ and HgI_2PCP one would expect no large differences in the Hg-I distances but a significant difference does exist in the former.

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In the complexes $HgI_2(PPh_3)_2$ and HgI_2PCP one would expect no large differences in the Hg-I distances but a significant difference does exist in the former.

8.2 Mercury to phosphorus distances

Complex	Hg-nP Distances (Å)	n	Difference Δ (Å)	Δ/σ(Δ)	Ref.
HgI_2PSP	2.498(11) 2.531(12)	1 1	0.033	2.0	1
$HgI_2(PPh_3)_2$	2.574(3) 2.557(3)	1 1	0.014	3.3	4
HgI_2PCP	2.578(3)	2			5
$Hg(SCN)_2(PPh_3)_2$	2.489(3) 2.487(3)	1 1	0.002	0.5	19

The agreement between the Hg-P distances within the different complexes is excellent. The distances in the SCN-complex is somewhat shorter than the corresponding distances in the iodine complexes. This may be caused by the difference in size between iodine and sulphur.

8.3 Silver to halogen distances

Complex	Ag-nX Distances (Å)	n		n	Differences Δ (Å)	Δ/σ(Δ)	Ref.
$(AgClPSP)_2$	2.656(4) 2.643(4)	1 1			0.013	23	2
$(AgIPSP)_2$			2.879(1) 2.911(1)	1 1	0.032	23	17
$[Ni(en)_2][AgI_2]_2$			2.895(1) 2.845(2) 2.863(2)	1 2 1	0.040	18	20

The Ag-Cl and Ag-I distances are somewhat longer than those calculated, from the tetrahedral covalent radii, [21] 2.51 and 2.63 Å, respectively. This is perhaps a result of a repulsion between silver and the chlorine atoms in the bridges.

8.4 Silver to phosphorus distances

Complex	Ag-nP Distances (Å)	n	Difference Δ (Å)	Δ/σ(Δ)	Ref.
$(AgClPSP)_2$	2.481(4) 2.461(4)	1 1	0.020	3.5	2
$(AgIPSP)_2$	2.461(2) 2.461(2)	1 1	0.000	0.0	17
$C_6H_5C\equiv CAgP(CH_3)_3$	2.490(4)	1			22
$Ag(SCN)P(C_3H_7)_3$	2.48(3)	1			23

The agreement between the complexes is excellent; differences between them Ag-P distances being hardly significant. However, they are about 0.15 Å shorter than the values calculated from tetrahedral radii.[21]

8.5 Nickel to halogen distances

Complex	Coordination number of Ni	Distance Ni-X(Å)	Difference Δ (Å)	Δ/σ(Δ)	Ref.
NiI_2PSP	5	2.794(2) 2.542(2)	0.252	89	3
$NiBr_2PNP$	5	2.698(7) 2.333(7)	0.365	37	14
$NiCl_2POP$	4	2.229(5) 2.210(4)	0.019	3.0	15
$NiBr_2(PPh_3)_2$	4	2.346(3) 2.329(3)	0.017	4.0	24

When the third donor atom in the ligand coordinates the metal atom, one of the nickel-halogen distances is increased. This can be seen by comparing the two bromine complexes.

8.6 Nickel-phosphorus and nickel-sulphur distances

Complex	Coord. number of Ni	Distance Ni-S (Å)	Distance Ni-nP (Å)	n	$\Delta/\sigma(\Delta)$	Ref.
NiI_2PSP	5	2.190(3)	2.192(3) 2.185(3)	1 1	1.6	3
$NiBr_2PNP$	5		2.172(5)	2	--	14
$NiBr[P(o\text{-}C_6H_4SCH_3)_3]_2$	5	2.789(10) 2.189(9)	2.120(9)	1	45	25
$NiCl_2POP$	4		2.309(4) 2.321(3)	1 1	2.4	15
$NiBr_2(PPh_3)_3$	4		2.323(5) 2.343(5)	1 1	2.8	24

The nickel-sulphur distance in NiI_2PSP is in good agreement with the shorter nickel-sulphur distance in $NiBr_2[P(o\text{-}C_6H_4SCH_3)_3]_2$. The second Ni-S distance in the latter is much larger due to the five-coordination.

More striking is the difference between the nickel-phosphorus distances in four- and five-coordinated complexes. When the coordination number is increased from four to five the Ni-P distance is decreased by about 0.15 Å. The mean value for the Ni-P distances for five-coordination is 2.17 Å and for four-coordination 2.32 Å.

9. CONCLUDING REMARKS

A comparison of measured metal to donor atom distances with the sums of their covalent radii reveals differences which may be related to the actual ring sizes and the stability of those rings.

In the eight-membered rings the metal to phosphorus distances are in relatively good agreement with the tetrahedral covalent radii sums. This is also the case for the metal to halogen distances in these complexes. From this it can be concluded that the eight-membered ring neither increases nor decreases the stability of the complexes.

During crystallisation either a chelate complex or a complex containing endless chains may be formed. Perhaps HgI_2PSP could crystallise in the form of endless chains, and HgI_2PCP in the form of a chelate complex.

When the third donor atom in the chelating ligand is also coordinated to the metal atom a large decrease in the metal-phosphorus distance is observed. This must be a result of the extremely high stability of the fused five-membered rings. These increase the stability so much that the Ni-P bond distances in the five-coordinated complex are 0.15 Å less than the value for tetrahedral coordination. At the same time one of the other two distances in the five-coordinated conformation is greatly increased.

In the dimeric $(AgXPSP)_2$ complexes the Ag to P distances are also decreased by about 0.15 Å compared to the tetrahedral radii sum. Dimerization with ten-membered bridging rings consequently increases the stability of the complex, in spite of the presence of the large rings.

10. ACKNOWLEDGEMENTS

I wish to express my sincere gratitude to Professors Sten Ahrland, Sture Fronæus and Gerold Schwarzenbach for their continuing interest in my work.

I am deeply indebted to Professor Bengt Aurivillius who introduced me to the field of X-ray crystallography. I owe him much for his suggestions and his valuable criticism.

Foremost I want to thank Dr. Karin Aurivillius for her excellent supervision, and for many valuable discussions during my work.

I also want to express my great appreciation of the help I have obtained from former and present colleagues at the Chemical Center.

This work has been sponsored by the Swedish Natural Research Council.

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